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(21) International Application Number: PCT/DK94/00437 (22) International Filing Date: 23 November 1994 (23.11.94) (30) Priority Data: 1311/93 23 November 1993 (23.11.93) DK (71) Applicant (for all designated States except US): NOVO NORDISK A/S [DK/DK]; Novo Allé, DK-2880 Bagsværd (DK). (72) Inventors; and (75) Inventors/Applicants (for US only): SHARYO, Masaki [JP/JP]; Takamidai Terrace House, 365-1, Yatsugasaki, Matsudo-shi, Chiba-ken 270 (JP). SHIMOTO, Hidesato [JP/JP]; 14-24, 1-chome, Kouyadai, Funabashi-shi, Chiba-ken 274 (JP). SAKAGUCHI, Hiromichi [JP/JP]; 1165-31, Yasashido-cho, Midori-ku, Chiba-shi, Chiba-ken 267 (JP). (74) Common Representative: NOVO NORDISK A/S; Att.: Corporate Patents, SLK, Novo Allé, DK-2880 Bagsværd (DK).		(81) Designated States: AM, AU, BB, BG, BR, BY, CA, CN, CZ, EE, FI, GE, HU, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LV, MD, MG, MN, MW, NO, NZ, PL, RO, RU, SD, SI, SK, TJ, TT, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ). Published <i>With international search report.</i>
(54) Title: DEINKING OF WASTE PAPER BY TREATMENT WITH STARCH DEGRADING ENZYME E.G. AMYLASE		
(57) Abstract <p>In the production of pulp and paper from starch-coated paper, the deinking effect can be improved by including a treatment with a starch-degrading enzyme e.g. amylase or a debranching enzyme. The process comprises enzyme treatment before, during or after disintegration of the paper to produce pulp, followed by separation of ink particles.</p>		

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Deinking of waste paper by treatment with starch degrading enzyme e.g. amylase

TECHNICAL FIELD

This invention relates to processes for producing a papermaking pulp and producing new paper from old starch-coated printed paper. More particularly, 5 it relates to such processes with improved ink removal leading to improved brightness of the pulp or paper.

BACKGROUND ART

In the recycling of old starch-coated printed paper such as old newspapers and magazines for use in papermaking, it is usually desirable to remove 10 the printing ink in order to produce new paper of high brightness. It is therefore conventional to repulp (or disintegrate) the old paper together with deinking chemicals, such as deinking surfactant, NaOH and sodium silicate, followed by bleaching with hydrogen peroxide and deinking chemicals and by separation of ink particles from the pulp.

15 A number of documents in the prior art describe the use of enzymes to improve ink removal. Thus, Japanese laid-open patent application Kokai Sho 59-9299 (Kao), Japanese laid-open patent application Kokai Sho 63-59494 (Honshu Paper), Japanese laid-open patent application Kokai Hei 2-80683 (Oji Paper) and WO 91/14819 (Novo Nordisk) describe the use of a cellulase, i.e. an enzyme acting 20 on the cellulose fibers of paper. Japanese laid-open patent application Kokai Hei 2-160984 (Novo Nordisk) and Japanese laid-open patent application Kokai Hei 2-80684 (Lion) describe the use of a lipase, i.e. an enzyme acting on triglycerides in the printing ink.

It is the object of this invention to provide an improved process for 25 removal of printing ink for use in the recycling of old starch-coated paper.

STATEMENT OF THE INVENTION

Surprisingly, we have found that in the production of pulp and paper from starch-coated paper, the deinking effect can be improved by including a treatment with a starch-degrading enzyme.

5 Accordingly, the invention provides a process for producing a papermaking pulp from starch-coated printed paper, comprising the following steps:

- a) disintegrating the paper to produce a pulp,
- b) treating with a starch-degrading enzyme before, during or after step a), and
- 10 c) separating ink particles from the pulp after steps a) and b).

The invention also provides a process for recycling old starch-coated printed paper into new paper, comprising producing a pulp by the above process, followed by papermaking.

DETAILED DESCRIPTION OF THE INVENTION

15 Starch-coated printed paper

The process of the invention is applicable to the recycling of any kind of printed, starch-coated paper. Typical examples are old newspaper, magazines and printed stationery. The paper may contain mineral fillers such as calcium carbonate and clay.

20 The starch coating may consist of starch from any source and generally contains 20-30% of amylose and the balance amylopectin. Typical examples are corn starch, wheat starch, potato starch, rice starch and tapioca starch. Starch to be used as a coating material will generally be pretreated to achieve a limited hydrolysis by cooking with amylase or acid.

25 The starch coating may also consist of modified starch. Modified starches useful for paper coating include dextrin (e.g. white dextrin, canary dextrin

or British gum), acid-modified starch, oxidized starch (chlorinated starch), hydroxyethylated starch and cationic starch

The inks to be removed by the process of this invention include but are not limited to non-contact laser inks, xerographic toners, letterpress ink generally used in printing newsprint, magazine print, offset printing ink, ultraviolet or electron beam cured ink.

Disintegration

The disintegration step may be done in a conventional pulper, typically for 5-30 minutes at 3-30% pulp consistency. If the enzyme treatment is completed before the disintegration, conventional deinking chemicals can be used in the disintegration.

Conventional deinking chemicals typically comprise an alkaline reagent and a surfactant. The surfactant can, e.g., be used at a dosage of 0.2-0.6%. The surfactant is preferably nonionic, e.g. ethoxylated octyl or nonyl phenol or any of the nonionic surfactants disclosed in Park et al., 1992, Biotechnology and Bioengineering 39:117-120. The alkaline reagent may be NaOH (e.g. 0.2-5%) and/or sodium silicate (e.g. 0.4-5%). The alkaline reagents are usually added to a pH of 8-12. The deinking chemicals may further comprise magnesium sulfate, an organic solvent such as kerosene, and sodium sulfite.

If the enzyme treatment is done during or after the disintegration, it may be preferable to modify the addition of deinking chemicals (as described further below) in order to provide suitable conditions for the action of the enzyme, and particularly to reduce or avoid the addition of alkaline reagent to achieve a pH which is suitable for the enzyme action.

25 Starch-degrading enzyme

The starch-degrading or amylolytic enzyme is preferably an amylase, e.g. an α -amylase, a glucoamylase or a debranching enzyme. A single enzyme or a combination may be used, e.g. α -amylase together with glucoamylase and/or a debranching enzyme. It is preferred to carry out the enzyme treatment at an alkaline

pH in the range 6-10, preferably 8-10 and to use an enzyme which is alkaline stable and active in this range and preferably has optimum activity in this range.

Examples of preferred α -amylases are those derived from strains of *Bacillus*, e.g. *B. amyloliquefaciens* (*B. subtilis*), *B. licheniformis* or *B. stearothermophilus* and from strains of *Aspergillus*, e.g. *A. oryzae*. Examples of commercial products are BAN™, Termamyl®, Aquazyme Ultra™ and Fungamyl™ (products of Novo Nordisk A/S).

Glucoamylase derived from a strain of *Aspergillus niger* is preferred, e.g. the commercial product AMG (product of Novo Nordisk).

10 The debranching enzyme is preferably a pullulanase, particularly one derived from a strain of *Bacillus acidopullulyticus*, e.g. the commercial product Promozyme® (product of Novo Nordisk).

The process conditions are selected so as to increase the brightness of the pulp after the deinking and the brightness of the new paper. Suitable conditions for *Bacillus* amylase may be pH 4-10, 20-90°C, preferably pH 6-10, 40-70°C. Suitable conditions for *A. oryzae* amylase may be pH 3-8, 20-70°C. A suitable reaction time may be found in the range 10 min - 24 hours, particularly 10 min - 3 hours at an amylase dosage of 0.01-10 KNU/g dry matter (1 KNU = 1000 NU, unit defined in US 4,933,279), preferably 0.03-3 (or 0.06-6) KNU/g of dry matter.

20 Optionally, one or more other enzymes, such as lipase, cellulase, protease and/or hemicellulase, can be used together with the starch-degrading enzyme to further improve the deinking efficiency.

Stirring may optionally be used during the enzymatic treatment.

Enzyme treatment

25 As stated above, the enzyme treatment may be done before, during or after the disintegration, and these alternatives will now be discussed.

Enzyme treatment before disintegration

The treatment with a starch-degrading enzyme can be done before the disintegration, e.g. by soaking the paper, either as it is or after shredding or cutting, 30 in an aqueous solution of the starch-degrading enzyme. The bath ratio (i.e., the

weight ratio of the enzyme solution to the paper) is preferably above 10, and the enzyme treatment is preferably done in the presence of a surfactant. In the case of an α -amylase from *Bacillus* it is preferred to add alkaline reagents (typically NaOH and sodium silicate) to achieve a suitable pH, e.g. pH 8-10 (preferably 8-9).

5 Preferably, the enzyme treatment is followed by additional separation of ink particles before the disintegration. The subsequent disintegration may be done in a conventional manner in the presence of deinking chemicals.

 The disintegration may be followed by conventional bleaching with hydrogen peroxide and deinking chemicals before the ink separation. Preferably,
10 separation of ink particles is done both before and after the bleaching.

Enzyme treatment during disintegration

 Alternatively, the enzyme treatment may be done during the disintegration. In this case, the enzyme treatment may optionally be continued by holding the pulp after the disintegration.

15 The enzyme treatment is preferably done in the presence of a surfactant, and in the case of an α -amylase from *Bacillus* it is preferred to add alkaline reagents (typically NaOH and sodium silicate) to achieve a suitable pH, e.g. pH 8-10 (preferably 8-9).

 The disintegration and enzyme treatment may be followed by
20 conventional bleaching with hydrogen peroxide and deinking chemicals before the ink separation. Preferably, separation of ink particles is done both before and after the bleaching.

Enzyme treatment after disintegration

 The enzyme treatment may be done by adding enzyme to the pulp
25 after disintegration. In a preferred embodiment, this is done simultaneously with hydrogen peroxide bleaching, preferably in the presence of a surfactant. In the case of simultaneous bleaching and treatment with an α -amylase from *Bacillus*, it is preferred to add 0.5-2% H₂O₂ and alkaline reagents (typically NaOH and sodium silicate, e.g. 1-5% sodium silicate and 0.5-5% NaOH) so as to achieve pH 9-10. The

combined bleaching and enzyme treatment is preferably done at 30-60°C for 1-3 hours.

Separation of ink particles

After the disintegration and enzyme treatment, ink particles may be separated from the pulp in a conventional manner, such as by mechanical deinking, flotation, chemi-mechanical deinking, agglomeration chemistry (see e.g. McBride, Pulp and Paper, April 1994, Miller Freeman Publishers, San Francisco, p. 44), washing, cycles of dilution and filtration, treatment in hydrocyclones, or by a suitable combination of these.

10 Papermaking

After deinking according to the invention, the deinked pulp is generally mixed with other pulp, e.g. kraft pulp and mechanical pulp etc., before papermaking. The final papermaking step can be done in a conventional papermaking machine.

EXAMPLES

15 EXAMPLE 1

Enzyme treatment before disintegration with deinking chemicals

Two kinds waste paper were treated by the process of the invention: Printed fine paper, mainly containing kraft pulp, off-set printed, starch coated, 8 months aged. Japanese regular newspaper containing deinked pulp, mechanical pulp, kraft pulp etc., off-set printed, starch coated, 4 months aged at room temperature.

10 g of the waste paper was cut by a shredder, suspended in water at 1% concentration, 65°C, pH 7.2. α -amylase (Aquazyme Ultra) was added in an amount of 0.3 KNU/g paper, and the mixture was kept for 60 minutes without agitation.

Rinsing was done with 2 l of water, twice.

Disintegration was done in a laboratory mixer for disintegration of paper at 4% pulp concentration, 55°C for 10 minutes with the following deinking chemicals: 0.3% of surfactant (Liptool 160H, product of Nikka Kagaku KK, Japan), 0.5% NaOH and 0.8% sodium silicate.

5 Washing was done with 2 l of water, twice.

A paper sheet was made on an 80 mesh wire (16 cm diameter).

A control experiment was done by the same procedure, but without the enzyme treatment.

Brightness of the paper sheet was measured at 457 nm in a
10 spectrophotometer equipped with an integrating sphere. The results are given as brightness (standard deviation in parentheses) for the experiment according to the invention and for the control experiment, and the increase in brightness is calculated.

	Type of newspaper	Printed fine	Regular
	Aging time	8 months	4 months
15	Invention	57.9 (0.4)	38.3 (0.3)
	Control	54.8 (0.8)	36.6 (0.5)
	Increase	3.1	1.7

EXAMPLE 2

Enzyme treatment before disintegration without deinking chemicals

20 The same two types of old newspaper as in Example 1 were subjected to enzyme treatment, followed by disintegration, flotation and washing, as follows:

a) The old newspaper was cut approx. to 3 x 3 square cm and 100 g (dry substance) was weighed out. The paper was mixed with 1800 ml hot water (45 °C) and enzyme solution was added. The enzyme was α -amylase (Aquazyme Ultra)
25 at a dosage of 0.5 KNU/g of dry pulp, in 100 ml of buffer at pH 7 (Britton-Robinson, universal Buffer I).

b) The mixture was incubated in a plastic bag in a water bath at 50 °C for 30 min. and then disintegrated in a disintegrator at 45,000 rotations in 15 min at 45-50°C at pH 7 and pulp consistency 5%.

c) After dilution (to 0.5% pulp consistency), the pulp was replaced to
5 flotation cell and agitated for 20 min. by mixer. Flotation conditions were 50 °C, pH 7, 10 min., 2000 rpm for air flow. Ink coming up with bubbles was scratched out.

d) Washing was done by taking 4 L of pulp after the flotation and washing 1 L each at 50°C, pH 7 on an 80 mesh sieve and filling up to 2.5 L.

e) Paper sheets were made from pulp after the flotation and from pulp
10 after the washing in a conventional manner. The brightness of the paper sheets was measured in a spectrophotometer with a blue filter.

Control sheets were made by the same procedure, but without the enzyme addition. The results are given as brightness for the experiment according to the invention and for the control experiment, and the increase in brightness is
15 calculated.

Newspaper	Printed fine		Regular	
Aging time	6 months		3 months	
Brightness	After flotation	After washing	After flotation	After washing
Invention	62.9	68.5	46.3	52.7
20 Control	57.2	64.9	45.1	50.9
Increase	5.7	3.6	1.2	1.8

EXAMPLE 3**Enzyme treatment during and after disintegration without deinking chemicals**

Old newspaper was treated in the same manner as in Example 2, except that in step b), the mixture was first disintegrated (at the same conditions) and then incubated in a plastic bag (at the same conditions). The results were as follows:

Newspaper	Printed fine		Regular	
Aging time	6 months		3 months	
Brightness	After flotation	After washing	After flotation	After washing
10 Invention	61.2	67.2	46.9	52.3
Control	57.5	64.0	43.7	49.3
Increase	3.7	3.2	3.2	3.0

The results of the examples show a clear effect of the enzyme treatment, both before during and after the disintegration, both with and without deinking chemicals and with both kinds of waste paper tested.

CLAIMS

1. A process for producing a papermaking pulp from starch-coated printed paper, comprising the following steps:
 - a) disintegrating the paper to produce a pulp,
 - 5 b) treating with a starch-degrading enzyme before, during or after step a), and
 - c) separating ink particles from the pulp after steps a) and b).
2. The process according to the preceding claim wherein the enzymatic treatment is done at a pH in the range 6-10, preferably 8-10, and the starch-
10 degrading enzyme is alkaline stable.
3. The process according to either preceding claim wherein the starch-degrading enzyme is an α -amylase.
4. The process according to any preceding claim wherein the α -amylase is derived from a strain of *Bacillus*, preferably *B. amyloliquefaciens*, *B. licheniformis*
15 or *B. stearothermophilus*.
5. The process according to the preceding claim wherein the enzymatic treatment is done with an amount of α -amylase in the range 0.01-10 KNU/g of dry matter.
6. The process of Claim 1, wherein the enzyme treatment is done before
20 the disintegration.
7. The process of the preceding claim wherein the enzyme treatment is done in the presence of a surfactant.

8. The process of the preceding claim wherein the enzyme is an alkaline stable enzyme, preferably a *Bacillus* α -amylase, and the enzyme treatment is done in the presence of an alkaline reagent at a pH in the range 8-10, preferably 8-9.
9. The process of any of claims 6 - 8, further comprising shredding or
5 cutting of the paper before the enzyme treatment.
10. The process of any of claims 6 - 9, further comprising bleaching after the disintegration, but before the ink separation.
11. The process of any of claims 6 - 10, additionally comprising separation of ink particles after the enzyme treatment, but before the disintegration.
- 10 12. The process of Claim 1, wherein the enzyme treatment is done simultaneously with the disintegration.
13. The process of the preceding claim wherein the enzyme treatment and disintegration are done in the presence of a surfactant.
14. The process of the preceding claim wherein the enzyme is an alkaline
15 stable enzyme, preferably a *Bacillus* α -amylase, and the enzyme treatment is done in the presence of an alkaline reagent at a pH in the range 8-10, preferably 8-9.
15. The process of the preceding claim, wherein the enzyme treatment is continued after the disintegration.
16. The process of any of claims 12 - 15, comprising the following
20 sequential steps after the disintegration and the enzyme treatment:
separation of ink particles,
bleaching, and
separation of ink particles.

17. The process of Claim 1, wherein the enzyme treatment is done after the disintegration.
18. The process of the preceding claim wherein the enzyme treatment is done simultaneously with bleaching.
- 5 19. The process of the preceding claim wherein the enzyme treatment and bleaching are done in the presence of hydrogen peroxide and a surfactant.
20. The process of the preceding claim wherein the enzyme is an alkaline stable enzyme, preferably a *Bacillus* α -amylase, and the enzyme treatment is done in the presence of an alkaline reagent, preferably at a pH in the range 8-10,
10 preferably 9-10.
21. A process for making new paper from starch-coated printed paper, comprising producing a papermaking pulp by the process of any preceding claim, and making the new paper from the pulp.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/DK 94/00437

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: D21C 5/02, C12S 3/08 // D21C9/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: D21C, C12S

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

DERWENT WORLD PATENT INDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 4450043 (WILLIAM J. SCHULZ), 22 May 1984 (22.05.84), abstract --	1-21
A	DE, A1, 2636951 (GÜNTHER WAGNER PELIKAN-WERKE GMBH), 23 February 1978 (23.02.78), page 1, line 28 - page 2, line 5 --	1-21
A	Dialog Information Services, file 351, Derwent WPI, Dialog accession no. 003906198, WPI accession no. 84-051743/09, KAO CORP: "De-inking agent for regenerating waste paper contains cellulase and opt. surfactant", JP 59009299, A, 840118, 8409 (Basic) --	1-21

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

International application No.

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO, A1, 9220857 (CALL, HANS-PETER), 26 November 1992 (26.11.92), abstract --	1-21
A	WO, A1, 9114819 (NOVO NORDISK A/S), 3 October 1991 (03.10.91), abstract, cited in the application -- -----	1-21

INTERNATIONAL SEARCH REPORT
Information on patent family members

09/02/95

International application No.
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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